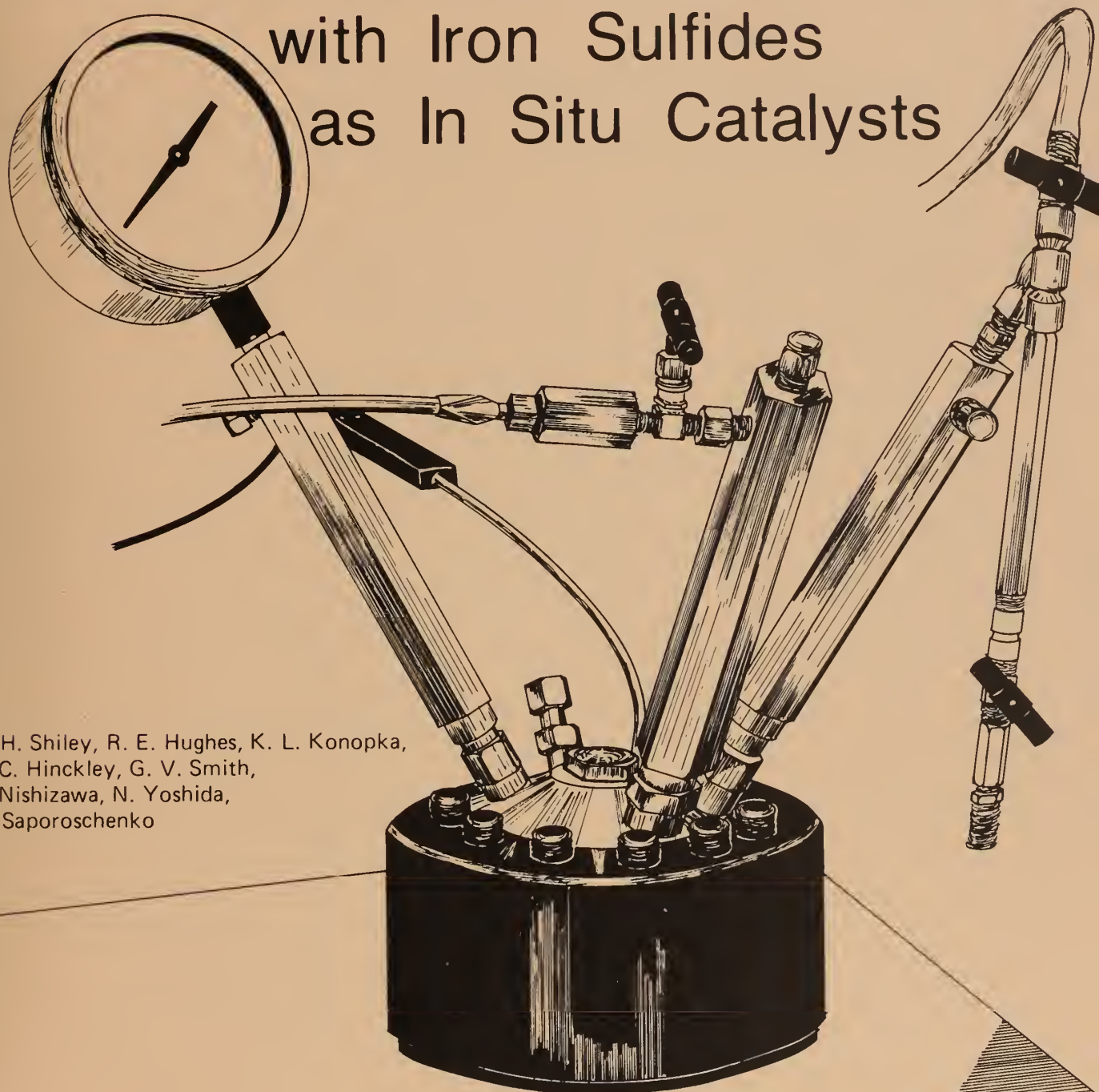


Design Principles for a Coal Desulfurization Process with Iron Sulfides as In Situ Catalysts

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Department of Energy and Natural Resources
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ABSTRACT

A pyrolytic desulfurization process that utilizes the catalytic properties of a troilite (FeS) / troilite "B" ($\text{Fe}_{16}\text{S}_{17}$) mixture prepared by the reduction and thermal transformation of pyrite and marcasite in coal matrix is currently under development for Illinois Basin high-sulfur coals. The first two steps or reactions in this sequence are (1) reduction of pyrite and marcasite by carbon monoxide to a troilite/troilite "B" mixture, which results in partial removal of sulfur and catalyzes further sulfur removal; and (2) conversion and removal of organic sulfur (as H_2S) with ethanol in the presence of the iron sulfide catalyst. Organic sulfur percentages have been reduced to less than 0.7 percent for most coals. Sulfur concentrations in the products are within the federal emission requirement of 1.2 pounds of sulfur dioxide per million Btu. Several coals have sulfur reductions that meet the 90 percent reduction in sulfur dioxide per million Btu requirement based on run-of-mine coal.

Flowing-gas conditions were found to be one of the most important design aspects of this process. Without these conditions, at the temperatures employed in this sequence, resulfurization by hydrogen sulfide (H_2S) and carbonyl sulfide (OCS) of the coal matrix produces a char with sulfur concentrations far above those required for compliance with federal emission standards. X-ray diffraction and Moessbauer spectroscopic methods were developed for the complete mineralogical characterization of the feed coal and the char produced at each step in the desulfurization process.

INTRODUCTION

A pyrolytic desulfurization process that uses the catalytic properties of a troilite (FeS) / troilite "B" ($\text{Fe}_{16}\text{S}_{17}$) mixture prepared by the reduction and thermal transformation of pyrite and marcasite in coal is currently under development for Illinois Basin high-sulfur coals.

The process is designed as a three-step reaction:

- pyrite and marcasite are reduced to a troilite/troilite "B" mixture by reaction with carbon monoxide; this reaction removes part of the sulfur as carbonyl sulfide (OCS) and prepares the way for the second step;
- ethanol is converted to acetaldehyde and hydrogen on the catalytic surface of the troilite/troilite "B" mixture; organic sulfur is converted to hydrogen sulfide and removed;
- the iron sulfide catalysts are removed by oxidation (this step has not yet been fully defined.).

With this process, organic sulfur percentages have been reduced to less than 0.7 percent for most coals. Sulfur concentrations in the products are within the federal emission requirement of 1.2 pounds of sulfur dioxide per million Btu. Several coals have sulfur reductions that meet the 90 percent reduction in sulfur dioxide per million Btu requirement based on run-of-mine coal.

Flowing-gas conditions are essential to this process. Without these conditions, resulfurization of the coal by hydrogen sulfide (H_2S) and carbonyl sulfide (OCS) produces a char with sulfur concentrations that exceed federal emission standards.

X-ray diffraction and Moessbauer spectroscopic methods were developed for the complete mineralogical characterization of the feed coal and the char produced at each step.

Previous research

Iron sulfides derived from pyrite and marcasite have been cited as possible aids in the desulfurization of coal (Eliot, 1978). We are developing a desulfurization process that uses iron sulfides as in situ catalysts. As a three-step sequence, this process is a distinct departure from its antecedents, which focus on a single desulfurization step. Our work, however, builds upon the successes of previous researchers.

In 1932, Snow reported the results of a desulfurization study that used several reactive gases to treat Illinois coals at elevated temperatures. Using hydrogen at 1000°C, Snow was able to remove 97 percent of the sulfur in coal; with carbon monoxide, he removed about 50 percent of the sulfur.

A recent compendium of methods to desulfurize coal before combustion cited 65 patents dealing with sulfur removal from coal and coke (Eliot, 1978). While some of these are ingenious cleaning methods, such as by water cyclones, electro-kinetics, and magnetic separation (Yan, 1977), most are chemical processes that use various additives and usually require heat and pressure. Some reactants used are gases, such as steam (Schroeder, 1975); hydrogen (Sinke, 1978); oxygen (Longanbach, 1977); nitrogen dioxide (Diaz and Guth, 1975); methane (Whitten et al., 1973), and various other mixtures. In addition to gases, reactants have included metal compounds, such as alkali carbonates (Stambaugh and Sachsel, 1977), iron oxide (Sanders, 1975), and ferric chloride (Meyers, 1973). Various solvents, including ethanol (Keller, 1977), are also used.

Almost all reported desulfurization techniques may be classified as first generation methods; most focus on a single step. Our process is considered second generation in that it builds on the successes of earlier researchers: the first step we apply is Snow's carbon monoxide treatment; then, ethanol treatment, which makes use of Keller's results (Keller, 1977); and, finally, oxidation of pyrrhotite to remove the original catalysts. The unique feature of the process is the application of the chemical and mineralogical properties of iron sulfides to catalyze sulfur removal.

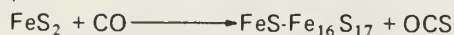
EXPERIMENTAL PROCEDURE

The first two steps of the process are the desulfurization sequence. The third step is the oxidation to remove the catalysts. This paper presents two experimental approaches to these first two steps of the process. In both systems, the reaction sequence is essentially the same (fig. 1).

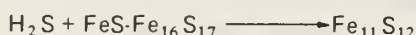
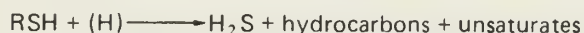
The proposed oxidation reactions in this process (step 3) have not been optimized for sulfide removal and carbon preservation. Therefore, as a convenient laboratory method of pyrrhotite removal, the chars were washed with hydrochloric acid and then extracted with methylene chloride to remove elemental sulfur formed during HCl washing.

DESULFURIZATION

Step 1



Step 2



OXIDATION

Step 3



Figure 1. Reactions of the three-step desulfurization process.

Comparison of experimental systems

The first two steps of our process, the desulfurization sequence, were investigated with two different experimental systems. Both the methods and the equipment varied in each system. In the first system, the carbon monoxide treatment (fig. 1, step 1) is carried out with gas flowing through the autoclave; the ethanol is reacted with the coal (fig. 1, step 2) in a closed autoclave under static conditions. The second, or modified system, involves the same two reactions. In this system, however, flow conditions are simulated in the ethanol reaction by repeated replacements of the ethanol. The results of the two approaches are presented in table 1.

Table 1. Desulfurization of Illinois coals

Location in Illinois	Coal seam no.	Pyritic sulfur wt %	Organic sulfur wt %	Total sulfur* wt %	Total sulfur in wt % in desulfurized product	
					First method	Modified method
Northwestern	2	1.33	0.96	2.71	0.39	—
West central	6	1.18	2.71	4.21	1.22	0.60
West central	6	1.21	2.89	4.37	—	0.42
Southwestern	6	1.37	2.08	3.56	0.86	0.45
Southwestern	6	0.63	1.79	2.50	—	0.47
Southwestern	5	1.22	2.11	3.47	—	0.52
South central	6	0.38	0.50	0.89	0.37	—
Southeastern	5	1.41	1.71	3.15	1.10	0.66

Note: No. 2 is the Colchester (No. 2) Coal Member, No. 5 is the Springfield (No. 5) Coal Member, and No. 6 is the Herrin (No. 6) Coal Member. The samples were collected as fresh material at the mine (except West Central No. 6 and Southeastern No. 5, which were preparation plant samples) and stored under an argon atmosphere, but are not necessarily representative of the mine product.

*Total sulfur includes unlisted sulfur present in the sulfate form.

A different Parr pressure reactor was specially designed for each system. The pressure reactor used in the first system has a capacity of 1000 ml and a capability of attaining temperatures up to 400°C. The pressure reactor used in the modified system has a capacity of 1000 ml and a capability of working temperatures of 700°C. Reaction conditions for both systems are summarized in table 2.

Table 2. Summary of reaction conditions for experimental approaches to desulfurization sequence

FIRST SYSTEM
<ul style="list-style-type: none">50 g coal heated at 250°C (up to 8 h) under flowing carbon monoxide at 200 cm³ /minReaction mixture cooled; carbon monoxide replaced with nitrogen, 18 g ethanol added, and mixture heated to 350°C for 5 h with autoclave sealed
MODIFIED SYSTEM
<ul style="list-style-type: none">50 g coal heated to 300°C 1 h, then run at 375°C (4 h) under flowing CO at 200 cm³ /min and 300 psi back pressureReaction mixture cooled; carbon monoxide replaced with nitrogen, 18 g ethanol added, and mixture heated to 350°C: ethanol replaced 4 times with 9 g each time (350°C, 400°C, 450°C, 550°C), then heated at 550°C for 4 h

Table 3. Ethanol removed during the reaction for southeastern Illinois Springfield (No. 5) Coal

Ethanol replaced (no. of times)	Total sulfur remaining (wt %)
0	1.00
4	0.71
5	0.66

The modified system for steps 1 and 2 simulates a flow system, such as that used in early pyrolysis and trace metal studies (Cahill, Shiley, and Shimp, 1982). To test the effectiveness of this system, an experiment was designed to remove the ethanol desulfurization products several times during the reaction (table 3). This experiment tested the assumption that carbonyl sulfide and hydrogen sulfide react rapidly with coal char to form stable organic sulfur compounds. Carbonyl sulfide and hydrogen sulfide were found to react with pure carbon to produce residues containing 3 percent and 8 percent sulfur, respectively. These results were consistent with those reported by other researchers for sulfur/hydrogen sulfide back reactions (Kor, 1977; Boodman, Johnson, and Krapinski, 1977).

Condensable products

Condensable products were collected in a dry ice trap during the desulfurization sequence: the carbon monoxide and ethanol steps. As a convenient method of oil collection from the trapping system, the condensed oil products were dissolved in acetone. This solution was evaporated at 100°C to constant weight. During this oil recovery process, volatiles with low boiling points (<100°C) were lost. They are not accounted for in our mass balance calculations.

Carbonyl sulfide production was measured during the carbon monoxide step using a static reaction system rather than the normal flow system. Gases were collected, sampled, and the carbonyl sulfide concentrations determined using a 1/8 in. x 1 ft (3mm x 0.3m) Teflon column packed with Poropac-QS in a Perkin Elmer Sigma I GC system. The conditions were as follows: injection port, 200°C; thermal conductivity detector (TCD), 200°C; flow rate, 30 ml/min; oven, set at 60°C isothermal. Carbonyl sulfide concentrations determined in a static reaction system will generally be lower than expected due to the resulfurization reaction of char by carbonyl sulfide.

Moessbauer spectroscopy

Moessbauer spectra were obtained with an Austin Science Associates Spectrometer that uses a linear acceleration motor to move the source (^{57}Co in Rh). A Nicolet 1070 N Signal Averager with 1024 channels collects the spectra. Two spectra were collected simultaneously and combined to yield a composite spectrum that was recorded in 512 channels. All spectra were obtained at room temperature and recorded until approximately 5×10^6 counts per channel had been accumulated in the base line. The spectra were analyzed by least squares fit of Lorentzian-shaped multiplets to the observed spectrum, using the computer program MOSFIT (Smith et al., 1978). Moessbauer spectra for the reaction products are shown in figure 2. These spectra show clearly the increasing degree of complexity and nonregularity of peak intensity ratios observed in the samples from the first two steps.

X-ray diffraction

X-ray diffraction (XRD) analyses were made with a Philips-Norelco diffractometer, which has a graphite-crystal monochromator to filter out secondary fluorescent radiation. Powder samples were scanned at a speed of 1 or 2° 2 θ /min, using copper radiation. Pyrrhotites

were characterized with respect to stoichiometry and crystal structure by comparing their XRD patterns with those of carefully prepared standard samples (table 4). Their crystal structure and stoichiometry were determined by using the most intense pyrrhotite XRD peak (fig. 3). The position of this peak is sensitive to pyrrhotite composition. For example, as the mole percentage of iron in pyrrhotite decreases, the 2θ peak position increases from 43.2° (FeS) to a maximum of 44.0° (Fe_7S_8).

Troilite "B," which is defined by us as the pyrrhotite with a composition about $\text{Fe}_{16}\text{S}_{17}$ is considered a mixture of troilite and hexagonal pyrrhotite.

Sample collection and preparation

Coal samples were collected at the mine and immediately stored in a canister under an argon atmosphere. Samples used in desulfurization experiments were ground in a glove box under an oxygen-free atmosphere to pass a U.S. 200-mesh standard sieve. After reaction, the chars were ground to pass a U.S. 60-mesh standard sieve before elemental, X-ray diffraction, and Moessbauer analysis.

RESULTS AND DISCUSSION

In the first step of the desulfurization process, pyrite and marcasite react with carbon monoxide to form carbonyl sulfide and a mixture of troilite and troilite "B." In the second step, the catalytically active troilite/troilite "B" mixture reacts with ethanol to form atomic

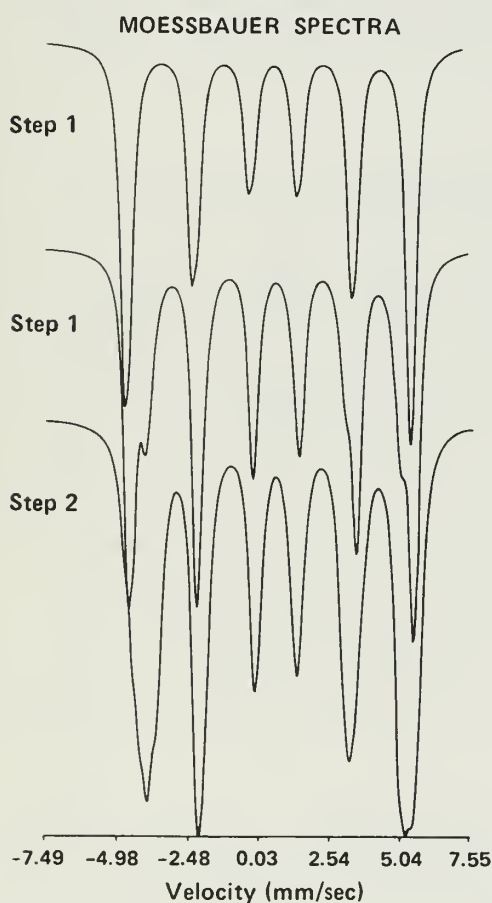


Figure 2. Moessbauer spectra of iron sulfide products from steps 1 and 2.

X-RAY DIFFRACTION PATTERNS FOR PYRRHOTITES

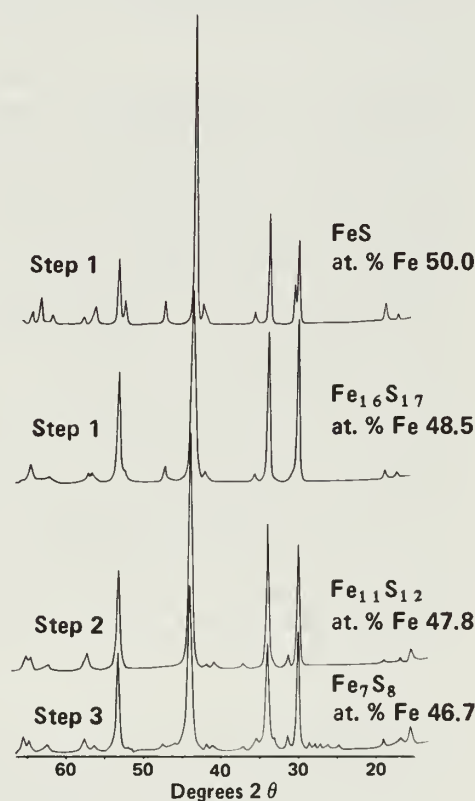


Figure 3. X-ray diffraction patterns of pyrrhotites.

Table 4. Mineral standards determined by X-ray diffraction

Species	Composition	Type	Mole % Fe	Magnetic properties	Source
Pyrite	FeS ₂	C	33.3	—	natural
Marcasite	FeS ₂	H	33.3	—	natural
Anomalous pyrrhotite	Fe ₆ S ₇	M	46.2	weak	from pyrite
Pyrrhotite 4C	Fe ₇ S ₈	M	46.7	strong	from pyrite
Pyrrhotite 5C	Fe ₉ S ₁₀	H	47.4	weak	from pyrite
Pyrrhotite 6C	Fe ₁₁ S ₁₂	H	47.8	—	from pyrite
Troilite “B”	Fe ₁₆ S ₁₇	H	48.5	—	from pyrite
Troilite 2C	FeS	H	50.0	—	from pyrite

Note: (C) = Cubic, (H) = Hexagonal, and (M) = Monoclinic type

hydrogen (H⁰). The hydrogen, in turn, reacts with organic sulfur compounds in the coal to form hydrocarbons, unsaturates, and hydrogen sulfide. The volatile sulfur compounds react with troilite to form hexagonal pyrrhotite (Fe₁₁S₁₂).

An important aspect of this desulfurization process is that pyrite and marcasite from coal are transformed to pyrrhotite without the production of elemental sulfur, which forms when pyrite is thermally decomposed (Morimoto, 1970). A central problem in this pyrolytic desulfurization procedure is the recombination of hydrogen sulfide and carbonyl sulfide (resulfurization or back reaction) with char. Under flowing-gas conditions, H₂S and OCS from pyrite and marcasite are carried out of the system. This removal prevents the recombination of H₂S and OCS with char.

First system Sulfur contents obtained for steps 1 and 2, using the first system, are shown in figure 4. The organic sulfur concentration of the Springfield (No. 5) Coal from south-eastern Illinois was not reduced to less than 1 percent.

In step 1, a carbon monoxide gas purge was used to remove carbonyl sulfide; whereas static reaction was the basis of step 2. To catalyze the removal of organic sulfur, step 2 makes use of the reactivity of ethanol with the troilite/troilite “B” mixture (Smith et al., 1984). Atomic hydrogen produced on the iron sulfide surface combines with organically bound sulfur to form hydrogen sulfide. Accompanying these reactions, sulfur is returned to the catalyst to form pyrrhotites, such as hexagonal pyrrhotite, which contain a higher sulfur-to-iron ratio than troilite or troilite “B.” During step 2, inorganic sulfur, organic sulfur, and hydrogen sulfide are thought to form a complex equilibrium, which is exploited to remove organic sulfur from the coal. When flowing-gas conditions were simulated by repeated exchanges of ethanol and removal of volatile sulfur-containing products in the autoclave gases, the composition of the iron sulfide in the coal was driven toward troilite. At the same time, the organic sulfur content of the chars fell, and the amount of sulfur removed increased with the number of times the ethanol was exchanged. All the fundamental reactions of the process are well known (Attar, 1978). In other research (Smith et al., 1982, 1984) we have shown that pyrrhotites will desulfurize thiols and that troilite will desulfurize thiophene.

Modified system With the modified system and frequent changes of the autoclave gases to simulate flow conditions, process conditions changed dramatically. The sulfur concentration of a southeastern Illinois coal was lowered to 0.66 percent (fig. 5). Mass balance calculations (table 5) for this experiment show that the sulfur remaining in the char is essentially equal to the calculated percentage of organic sulfur (0.65%).

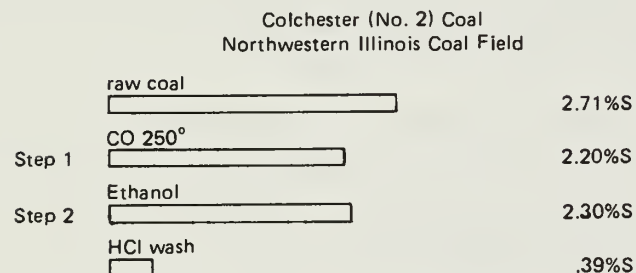
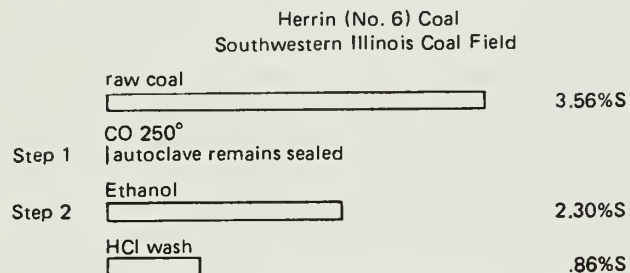
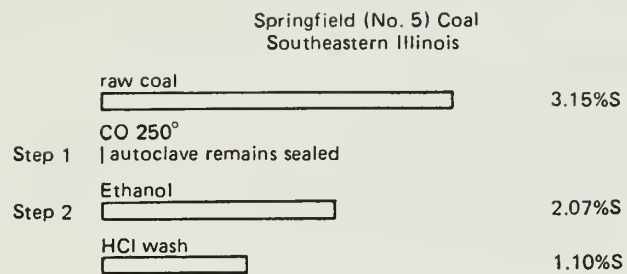


Figure 4. Sulfur content for steps 1 and 2 using the first system.

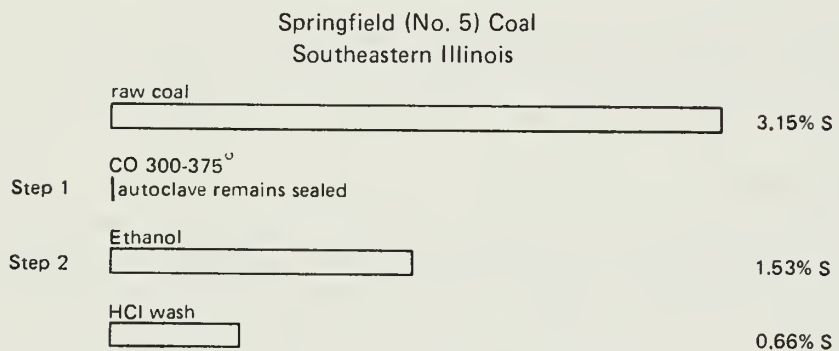


Figure 5. Sulfur content for steps 1 and 2 using the modified system.

Table 5. Mass balance for southeastern Illinois
Springfield (No. 5) Coal desulfurization

Whole coal analysis	Char (ethanol treatment) analysis
Sample weight 50 g	Sample weight 39.7 g
Total sulfur 3.15%	Total sulfur 1.53%
Pyritic sulfur 1.41% or 0.71 g	Pyrrhotitic sulfur 0.88% or 0.35 g
Organic sulfur 1.71%	Organic sulfur 0.65% (calculated) Organic sulfur 0.66% (actual)

The mass balance (table 5) includes several steps that trace the preservation or elimination of various forms of sulfur during treatment. In this example, the starting coal contains 1.41 percent pyritic and 1.71 percent organic sulfur. The starting sample weight was 50 g, which included 0.712 g of pyritic sulfur. After charring, the sample weight decreased to 39.7 g, and the char contained 0.35 g (0.88%) pyrrhotitic sulfur (based on converting all the pyrite to pyrrhotite with a composition of about 50 at. % iron or $\text{FeS}/\text{Fe}_{16}\text{S}_{17}$). Given a total sulfur content of 1.53 percent, the organic sulfur content of the char equals the total sulfur minus pyrrhotitic sulfur (1.53% to 0.88%) or 0.65 percent. When the char was actually washed with HCl and methylene chloride to remove pyrrhotitic sulfur, the total sulfur dropped to 0.66 percent. The excellent match between calculated and observed organic sulfur content indicates clearly that further sulfur removal can only be achieved by process modifications that will increase organic sulfur removal. The compositions of the desulfurization products are summarized in table 6.

Table 6. Properties of the desulfurized products of southeastern Illinois
Springfield (No. 5) Coal

Char

Weight: approximately 80% of original sample
Analysis: 0.66% sulfur content; 12.200 Btu/lb heating value

Carbonyl Sulfide

Weight: approximately 20% of theory based on pyrite/marcasite content

Oil

Volume: 0.4 bbl/ton of coal after evaporation at 100°C
Characteristics: stable in air (with polymerization); soluble in organic solvents

CONCLUSIONS

This process manipulates the sulfur equilibrium in response to catalysis of iron sulfides and reactor flow conditions to remove organic sulfur. The importance of flowing-gas conditions in the desulfurization process is a central finding of this research. Simulated flow conditions produce significantly greater sulfur removal in this process. At the temperatures used, reaction of elemental sulfur, carbonyl sulfide, and hydrogen sulfide gases with the carbon phase of the coal is significant. It is important, therefore, to ensure that sulfur and hydrogen sulfide or carbonyl sulfide produced in the first two steps are removed from the system before they have an opportunity to recombine with the coal. Resulfurization of this kind is a severely limiting factor in many desulfurization processes. A concomitant effect of the flowing-gas conditions in the ethanol step is that the composition of the iron sulfide in the coal is driven toward troilite, FeS . Troilite appears to facilitate the removal of thiophenic sulfur.

Our desulfurization process resulted in the production of several desulfurized chars that meet federal emission compliance standards (table 1). Sulfur removal to this degree was made possible by the discovery of several principles that greatly affect the removal of organically bound sulfur from the coal matrix.

- The coal must be fresh. Reaction of the coal with oxygen limits the effectiveness of this process.
- About 50 percent of the sulfur present in the form of pyrite (FeS_2) must be removed as carbonyl sulfide (OCS) at temperatures below those at which pyrite thermally decomposes to avoid the formation of elemental sulfur that accompanies the thermal decomposition of pyrite to pyrrhotite.

Required reaction: $\text{FeS}_2 + \text{CO} \longrightarrow \text{FeS} + \text{OCS (gas)}$

Deleterious reaction: $\text{FeS}_2 \longrightarrow \text{Fe}_{1-x}\text{S} + \text{S}^0$

- Troilite is a more effective catalyst than pyrite, marcasite, or other members of the pyrrhotite group for the hydrogenation and removal of stable sulfur forms, such as those found in chemical analogs of thiophene. Thus, the proportion of troilite relative to other members of the pyrrhotite group is a significant factor in the effectiveness of our process.
- Flowing-gas conditions provide the means necessary to avoid recombination of sulfur products with coal. Moreover, this removal of sulfur favors the formation of troilite, which catalyzes the liberation of thiophenic sulfur.

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REFERENCES

- Attar, A., 1978, Chemistry, thermodynamics and kinetics of reaction of sulfur in coal-gas reactions: a review: *Fuel*, v. 57, p. 201-212.
- Boodman, N. S., T. F. Johnson, and K. C. Krupinski, 1977, Fluid bed carbonization/de-sulfurization of Illinois coal by the clean coke process: PDU studies, *in* Wheelock, T. O. [ed.], *Coal Desulfurization, Chemical and Physical Methods*, A.C.S. Symposium Series 64, p. 248.
- Cahill, R. A., R. H. Shiley, and N. F. Shimp, 1982, Forms and volatilities of trace and minor elements in coal, I. A comparison of three pyrolysis units: *Illinois State Geological Survey Environmental Geology Notes* 102, p. 1-22.
- Diaz, A. F., and E. D. Guth, 1975, U.S. Patent 3909211.
- Eliot, R. C. [ed.], 1978, *Coal desulfurization prior to combustion*: Noyes Data Corp., Park Ridge, N.J.
- Keller, L. J., 1977, U.S. Patent 4030893.
- Kor, G.J.W., 1977, Desulfurization and sulfation of coal and coal char, *in* Wheelock, T. O. [ed.], *Coal Desulfurization, Chemical and Physical Methods*, A.C.S. Symposium Series 64, p. 221.
- Loganbach, J. R., 1977, U.S. Patent 4054420.
- Meyers, R. A., 1973, U.S. Patent 3768988.
- Morimoto, N., H. Nakazawa, K. Nishiquchi, and N. Tokonami, 1970, Pyrrhotites stoichiometric compounds with composition $\text{Fe}_{n-1}\text{S}_n$ ($n \geq 8$): *Science*, v. 168, p. 964-966.
- Sanders, R. N., 1975, U.S. Patent 3909213.
- Schroeder, W. C., 1975, U.S. Patent 3909212.
- Sinke, G. C., 1978, U.S. Patent 4071328.
- Smith, G. V., J. Liu, M. Saporoschenko, and R. H. Shiley, 1978, Mossbauer spectroscopic investigations of iron species in coal: *Fuel*, v. 57, p. 41-45. *Illinois State Geological Survey Reprint Series* 1978E.
- Smith, G. V., C. C. Hinckley, O. Zahra, T. Nashizawa, M. Saporoschenko, and R. H. Shiley, 1982, Comment on the nature of iron sulfides during catalytic reactions: *Journal Catalysis*, v. 78, p. 262-263.
- Smith, G. V., C. C. Hinckley, T. Nishizawa, N. Yoshida, M. Saporoschenko, and R. H. Shiley, 1984, VIII International Conference Catalysis, West Berlin, Proceedings IV, 439.
- Snow, R. D., 1932, Conversion of coal sulfur to volatile sulfur compounds during carbonization in streams of gases: *Industrial and Engineering Chemistry*, v. 24, p. 903-909.
- Stambaugh, E. P., and G. F. Sachsels, 1977, U.S. Patent 4055400.
- Whitten, C. M., V. Mansfield, L. J. Petrovik, and J. C. Agarwall, 1973, U.S. Patent 3759673.
- Yan, T. Y., 1977, U.S. Patent 4052170.

